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THERMOCHEMICAL CHARACTERIZATION OF SOME THERMOPLASTIC MATERIALS

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ABSTRACT: The thermochemical and flammability characteristics of some typical thermoplastic materials currently in use and others being considered for use in aircraft interiors are described. The properties studied included (1) thermomechanical properties such as glass transition and melt temperature, (2) changes in polymer enthalpy, (3) thermogravimetric analysis in anaerobic and oxidative environments, (4) oxygen index, (5) smoke evolution, (6) relative toxicity of the volatile products of pyrolysis, and (7) selected physical properties. The generic polymers that were evaluated included: acrylonitrile butadiene styrene, bisphenol A polycarbonate, 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer, phenolphthalein-bisphenol A polycarbonate, phenolphthalein polycarbonate, polyether sulfone, polyphenylene oxide, polyphenylene sulfide, polyaryl sulfone, chlorinated polyvinyl chloride homopolymer, polyvinyl fluoride, and polyvinylidene fluoride. Processing parameters, including molding characteristics of some of the advanced polymers, are described. Test results and relative rankings of some of the flammability, smoke, and toxicity properties are presented. Under these test conditions, some of the advanced polymers evaluated were significantly less flammable and toxic or equivalent to polymers in current use.

INTRODUCTION

THERMOPLASTIC MATERIALS ARE used in aircraft interiors as decorative films, compression- and injection-molded parts, and thermoformed parts. Typical components include: passenger service units, luminaries, seat side panels, trays and shrouds, flight station and lavatory parts, and panel finish in the form of film. Even though currently used materials meet regulatory requirements [1] there is consider-

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able effort both by industry, aircraft manufacturers, and government to study and define materials that would offer improved fire resistance and, upon combustion, produce less smoke, irritating fumes, and toxic gases [2-13].

This study assessed the relative thermal stability, flammability, and other related thermochemical properties of some typical state-of-the-art and candidate experimental thermoplastic materials and assessed their potential use as moldings, thermoformed parts, and decorative films in aircraft interiors. State-of-the-art materials that were evaluated included: acrylonitrile butadiene styrene (ABS), bisphenol A polycarbonate (BPAPC), polyphenylene oxide (PPO), and polyvinyl fluoride (PVF).

Advanced thermoplastic materials evaluated included: 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer (BPFC-DMS), chlorinated polyvinyl chloride homopolymer (CPVC), phenolphthalein bisphenol A polycarbonate (PH-BPAPC), phenolphthalein polycarbonate (PHPC), polyethersulfone (PES), polyphenylene sulfide (PPS), polyaryl sulfone (PAS), and polyvinylidene fluoride (PVF₂).

EXPERIMENTAL

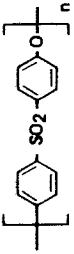
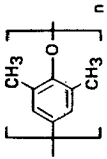
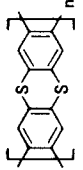
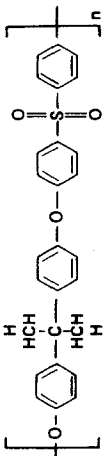
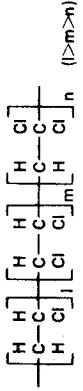
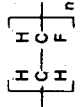
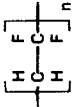
Description of Polymers

A total of 12 polymers and 23 samples were utilized for this study. The polymers were either commercially obtained or were experimental polymers being developed by various laboratories. The chemical structure of the polymers is shown in Table 1. Polymers were available as molding pellets, extruded or solvent cast film, extruded or molded sheet, and molding powders or pellets. The description for each polymer is also shown in Table 1. A brief description of polymers follows: acrylonitrile butadiene styrene, sample 18, was commercially obtained in sheet form. The chemistry of acrylonitrile butadiene styrene has been described previously [14]. Bisphenol A polycarbonate was available in two types: bisphenol A polycarbonate with no fire retardants (sample 14) and one with fire retardants (sample 19). 9,9-bis (4-hydroxyphenyl)-fluorene polycarbonate-poly (dimethylsiloxane) block polymer was evaluated as a clear film, (sample 21) as an uncured and cured molding powder (samples 27 and 28) and as injection-molded clear discs (sample 23). The poly (dimethylsiloxane) varied in the samples from 15% to 22%. The chemistry and synthesis of this polymer have been described previously [15-18]. The chemistry and synthesis of the phenolphthalein-bisphenol A polycarbonate copolymers (samples 30, 31, and 55) have been described previously [19]. Polyether sulfone was evaluated as molding pellets (samples 12 and 13) and extruded film (sample 22). The chemistry and synthesis of the polyether sulfone evaluated have been described previously [20]. Polyphenylene oxide was available in molded sheet (sample 16). The chemistry of polyphenylene oxide has been described previously [21]. Polyphenylene sulfide was evaluated as molding pellets (sample 11) and molded sheet (samples 20 and 24). Its chemistry has been described previously [22]. Polyaryl sulfone was evaluated as molding pellets (sample

Table 1. Typical Chemical Structures of Polymers.

SAMPLE NUMBER	SAMPLE DESCRIPTION	POLYMER	POLYMER STRUCTURE
18	SHEET	ACRYLONITRILE BUTADIENE STYRENE (ABS)	
14	SHEET	BISPHENOL A POLYCARBONATE (BPAPC)	
19	FIRE RETARDANT; SHEET		
21	FILM; SOLVENT CAST FROM CHLOROFORM, 21% DMS	9,9 BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYLSILOXANE) BLOCK POLYMER (BPFC-DMS)	
23	INJECTION MOLDED DISCS, 10.16 cm. DIA. by 0.3175 cm, 15% DMS		
27	UNCURED, MOLDING POWDER		
28	MOLDING POWDER, CURED AT 315.56° C		
30	80% MOLE PHENOLPHTHALEIN, FILM	PHENOLPHTHALEIN-BISPHENOL A POLYCARBONATE COPOLYMER (PH-BPAPC)	
31	70% MOLE PHENOLPHTHALEIN, FILM		
55	FILLED WITH 10% Al2O3, 5% TiO2; FILM	PHENOLPHTHALEIN POLYCARBONATE (PHPC)	

Table 1. Continued.

SAMPLE NUMBER	SAMPLE DESCRIPTION	POLYMER	POLYMER STRUCTURE
12 13 22	MOLDING PELLETS MOLDING PELLETS 0.0127 cm FILM	POLYETHER SULFONE (PES)	
16	MODIFIED; SHEET	POLYPHENYLENE OXIDE (PPO) (POLY-2,6-DIMETHYL- PHENYLENE OXIDE)	
11 20 24	MOLDING PELLETS MOLDED PART SECTION, 0.3175 cm THICK 0.3175 cm SHEET	POLYPHENYLENE SULFIDE (PPS)	
10 15	MOLDING PELLETS MODIFIED; SHEET	POLYARYLSULFONE (PAS)	
17 25	SHEET SHEET	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	
32	0.0051 cm FILM	POLYVINYL FLUORIDE (PVF)	
58	0.0127 cm FILM	POLYVINYLIDENE FLUORIDE (PVF2)	

10) and molded sheet (sample 15). Its chemistry has been described previously [23]. Chlorinated polyvinyl chloride homopolymer was evaluated as molded sheets (samples 17 and 25). The chemistry of this polymer has been described previously [24, 25, and 26]. Polyvinyl fluoride and polyvinylidene fluoride were evaluated as films (samples 32 and 58). The chemistry of these polymers has been described previously [27].

Processing of Polymers

Processing studies were conducted to determine the feasibility of processing the advanced polymers. The purpose was to evaluate processing parameters for molding and to optimize the parameters for molding specimens with optimum thermo-physical properties. Processing studies were conducted on 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane), polyether sulfone, polyphenylene sulfide, and polyaryl sulfone.

9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer was injection-molded using a Battenfeld 78.4 g reciprocating screw injection-molding machine. The granules of the polymer were dried prior to molding under vacuum at 130°C until no further weight loss was noted.

The following molding process parameters were utilized: the barrel temperature profile was set at the rear nozzle at 298°C, in the middle nozzle at 321°C, and at the front nozzle at 315°C. The mold temperature was 121°C; the mold surface temperature was 107°C. The injection pressure was 89635 kN/m², the injection speed 1 sec, the injection pressure hold-time 10 sec, the feed time 25 sec, the screw rpm was 160, and the pressure in the runner feeding disk was 7998 kN/m². Disks with good optical clarity (sample 23) were produced using the above molding procedure.

Molding of the other materials (polyether sulfone, polyphenylene sulfide, and polyaryl sulfone) was accomplished in a conventionally heated molding press using conventional compression molding techniques. All of the specimens were made in an aluminum mold consisting of a ring segment 1.905 cm long, 7.620 cm i.d., and 1.270 cm wall, screwed to a 0.953 cm flat plate. The ram, a 6.350 cm long solid aluminum rod, 7.620 cm in diameter, was machined for a slip fit into the ring. Molding parameters for these materials are summarized in Table 2.

Molding tests were made of polyether sulfone and polyphenylene sulfide to establish a workable temperature and pressure cycle that would form flat panels in a thickness range of 0.254 to 0.635 cm. All materials were in the form of pellets of about 0.381 cm long by 0.254 cm diam., and each had a melting point of approximately 260°C. Materials were kept in a 148°C oven and removed just prior to molding.

Polyether sulfone appears to have satisfactory molding characteristics for producing sheet stock. Initial trials were not successful because the pellets were not dried. Once the 148°C drying process was employed, satisfactory specimens could

Table 2. Typical Molding Parameters for Compression Molding of PES, PPS, PAS.

MOLDING PARAMETER	PES	PPS	PAS
MOLDING CYCLE:			
STABILIZE PRESSURE (minutes) RANGE OPTIMUM	3-5 4	3-8 5	2-10 4
MAINTAIN PRESSURE (minutes) RANGE OPTIMUM	5-7 5	4-10 5	4-30 6
MOLDING PRESSURE (MN/m ²) RANGE OPTIMUM	3.448-27.580 6.895	3.448-27.580 6.895	1.944-58.525 7.585
MOLDING TEMPERATURE (°C):			
INITIAL, RANGE OPTIMUM	232-316 274	260-289 277	340-370 347
FINAL, RANGE OPTIMUM	238-307 260	260-288 273	315-370 327
LOWEST DURING CYCLE, RANGE OPTIMUM	213-310 252	238-279 271	310-330 315

be provided over a reasonable range of temperature and pressure conditions, as shown in Table 2. Polyphenylene sulfide was slightly more difficult to mold into satisfactory specimens than polyether sulfone. The polyphenylene sulfide has a somewhat higher melting point than polyether sulfone (approximately 267°C). However, it becomes liquid at the melting temperature, and even low pressures force it out of the mold completely. Yet, at slightly lower temperatures, the material does not consolidate completely under very high pressures, i.e., 27.58 MN/m². Optimum molding conditions and satisfactorily molded specimens were obtained with a molding pressure of 6.8 MN/m² and molding temperature of 238° to 260°C. Polyaryl sulfone was molded satisfactorily also at a molding temperature of 399°C and a molding pressure of 13.5 MN/m².

RESULTS AND DISCUSSION

Thermochemical Characterization

The polymers were characterized for the following chemical properties: thermo-mechanical properties such as glass transition temperature (T_g), melt temperature (T_m), and char yield in anaerobic and oxidative environments.

Thermomechanical Properties: — The glass transition (T_g) and melt (T_m) temperatures were determined by the DuPont thermal mechanical analyzer (TMA), Model 441, with the DuPont thermal analyzer, Model 900. Measurements were made in the penetration or compression mode, using a hemispherical tip probe.

The materials that were studied included phenolphthalein-bisphenol A polycarbonate copolymer, polyether sulfone, polyphenylene sulfide, polyaryl sulfone, and polyvinylidene fluoride. The T_g and T_m data for these polymers are presented in Table 3, together with data of the other polymers.

The T_g and T_m data for acrylonitrile butadiene styrene, 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer, phenolphthalein polycarbonate, polyphenylene oxide, chlorinated polyvinyl chloride homopolymer, and polyvinyl fluoride indicated in Table 3 are from References 16, 19, 21, 28–32.

In addition to studies conducted on the TMA, differential scanning calorimetry (DSC) studies were conducted with a DuPont Model 900 DSC on polyphenylene sulfide, polyaryl sulfone, and polyether sulfone. In the DSC for polyether sulfone and polyaryl sulfone, an endotherm was observed when the temperature of thermal decomposition was attained.

The authors are aware that the DuPont Model 900 DSC is not truly a calorimeter but is more nearly designed to perform as a differential thermoanalyzer; it was, however, the only readily available apparatus to conduct these measurements.

The thermal properties of polyphenylene sulfide are shown in Figures 1 through 3. Two endotherms and one exotherm were observed. The DSC thermogram (Figure 1) shows an endotherm (a) at 90°C. This temperature corresponds to the

Table 3. Glass Transition Temperature (T_g) and Melting Temperature (T_m) of Thermoplastics.

SAMPLE NUMBER	POLYMER	RUN NUMBER	HEATING RATE ($^{\circ}\text{C}/\text{min.}$)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
18	ACRYLONITRILE BUTADIENE (ABS)	---	---	~ 80 (14)	---
14	BISPHEINOL A POLYCARBONATE (BPAPC)	---	---	150 (19)	263 (19)
19	9,9 BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYLSILOXANE) BLOCK POLYMER (BPFC-DMS)	---	---	150 (19)	263 (19)
21		---	---	~ 240	~ 360
23		---	---	~ 215	$\sim 360-370$
27		---	---	~ 215	$\sim 360-370$
28		---	---	---	---
30	PHENOLPHTHALEIN-BISPHEINOL A POLYCARBONATE COPOLYMER (PH-BPAPC)			~ 255	~ 278
31				~ 250	~ 260
55	PHENOLPHTHALEIN POLYCARBONATE (PHPC)	---	---	278 (19)	295 (19)
12	POLYETHER SULFONE (PES)	1	5	218	228
		2	15	220	228
		3	15	225	---
13		1	25	---	208
22		---	---	---	---

Table 3. Continued.

SAMPLE NUMBER	POLYMER	RUN NUMBER	HEATING RATE (°C/min.)	T _g (°C)	T _m (°C)
16	POLYPHENYLENE OXIDE (PPO)	---	---	~210 (21)	~257 (21)
11	POLYPHENYLENE SULFIDE (PPS)	1	15	89	271
		2	2	88	250
20		---	---	---	---
24	POLYPHENYLENE SULFIDE (PPS)	1	15	89	271
		2	15	92	275
		3	15	86	270
		4	15	82	260
		5	30	88	267
10	POLYARYL SULFONE (PAS)	1	15	283	310
		2	15	282	303
15	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	---	---	---	---
17		---	---	---	~195 (29)
25		---	---	---	~195 (29)
32	POLYVINYL FLUORIDE (PVF)	---	---	70 (30)	210 (31)
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	1	25	32	138
		2		50	148

Table 3. Continued.

SAMPLE NUMBER	POLYMER	RUN NUMBER	HEATING RATE (°C/min.)	T _g (°C)	T _m (°C)
18	ACRYLONITRILE BUTADIENE (ABS)	---	---	~ 80 (14)	---
14	BISPENOL A POLYCARBONATE (BPAPC)	---	---	150 (19)	263 (19)
19		---	---	150 (19)	263 (19)
21	9,9 BIS (4-HYDROXYPHENYL) FLUORENE	---	---	~240	~360
23	POLYCARBONATE-POLY (DIMETHYLSILOXANE) BLOCK POLYMER (BPFC-DMS)	---	---	~215	~360-370
27		---	---	~215	~360-370
28		---	---	---	---
30	PHENOLPHTHALEIN-BISPENOL A POLYCARBONATE COPOLYMER (PH-BPAPC)			~255	~278
31				~250	~260
55	PHENOLPHTHALEIN POLYCARBONATE (PHPC)	---	---	278 (19)	295 (19)
12		1	5	218	228
		2	15	220	228
		3	15	225	---
13	POLYETHER SULFONE (PES)	1	25	---	208
22		---	---	---	---

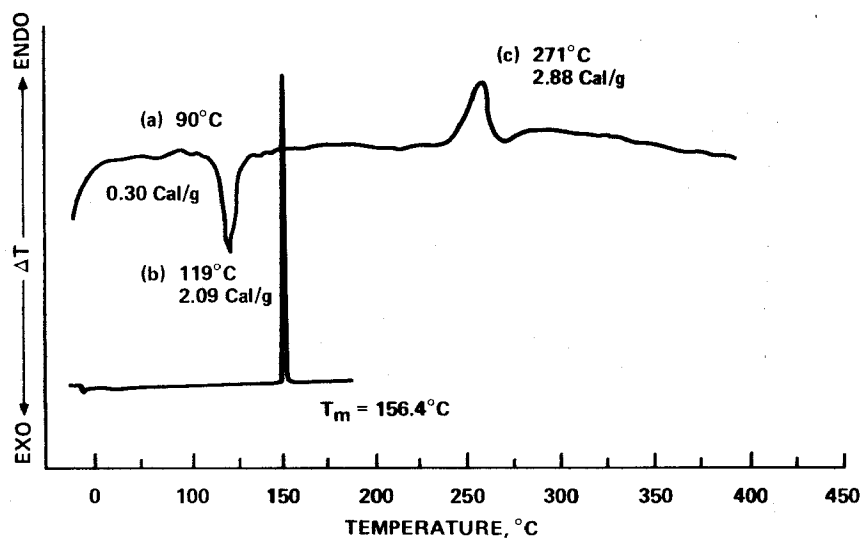


Figure 1. Thermal properties of polyphenylene sulfide (differential scanning calorimeter, heating rate = 10°C/min , air).

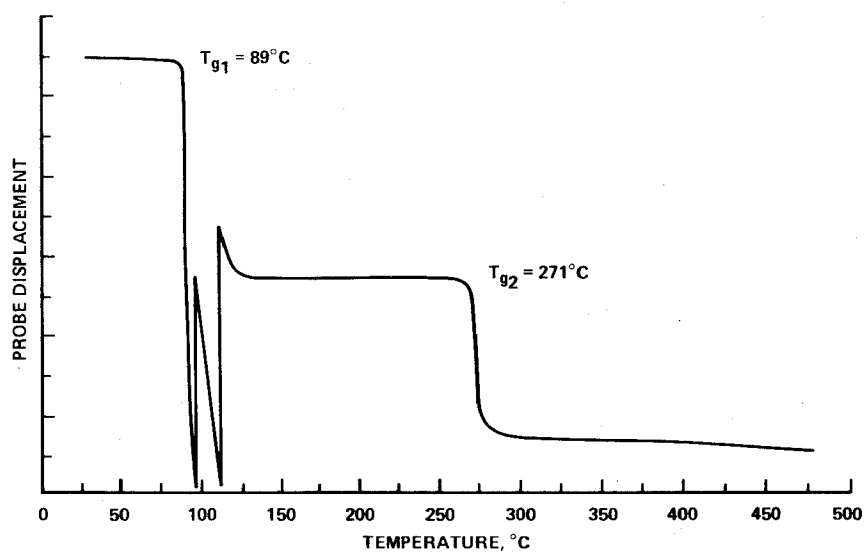


Figure 2. Thermal properties of polyphenylene sulfide (thermomechanical analysis-penetration, heating rate = 15°C/min , air).

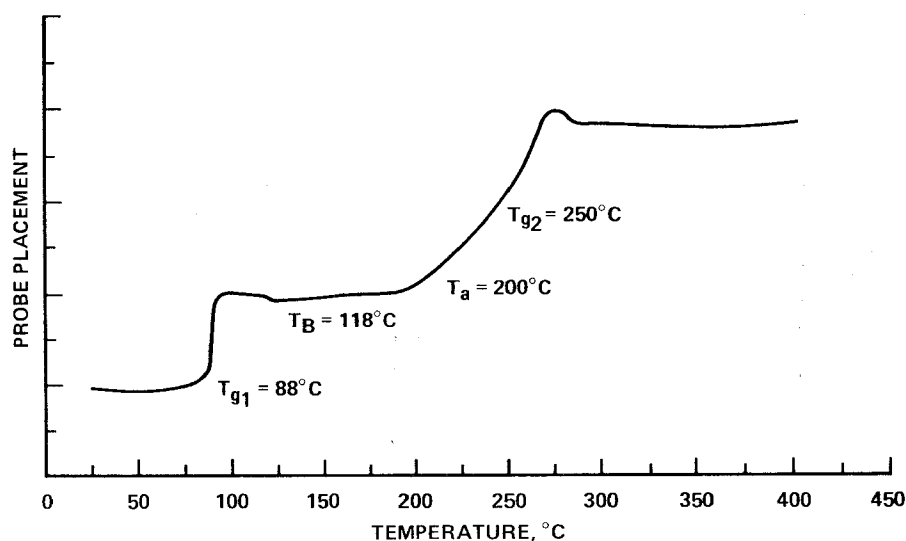


Figure 3. Thermal properties of polyphenylene sulfide (thermomechanical analysis-dilatometer, heating rate = $2^{\circ}\text{C}/\text{min}$, air).

glass transition temperature ($T_g = 89^{\circ}\text{C}$) determined by TMA as shown in Figure 2. However, an enthalpy change is not associated with T_g as it is not a first-order transition. Thus, the transition at 90°C must be due to melting, which is a first-order transition. This is confirmed by the dilatometer thermogram (Figure 3). The transition ($T_g = 88^{\circ}\text{C}$) is essentially isothermal. The data indicate that polyphenylene sulfide is highly crystalline. Previous studies [33] have shown a glass transition temperature of 85°C . The second endotherm, Figure 1(c) at 271°C , may be due to some thermal decomposition, even though this weight loss was not evident in the TGA thermogram because of the rapid heating rate ($40^{\circ}\text{C}/\text{min}$). The exotherm, Figure 1(b) at 119°C , is due to crosslinking of polyphenylene sulfide. According to previous studies [33], crosslinking with recrystallization occurs in the presence of air. Polyphenylene sulfide again forms a glass on crosslinking. This is evident from the very low coefficient of thermal expansion, as shown in Figure 3. The decrease in specific volume at $T_B = 118^{\circ}\text{C}$ indicates that the polymer shrinks on crosslinking.

A secondary transition T_a occurs at $T_a = 200^{\circ}\text{C}$, as shown in Figure 3. It is not detected by TMA penetration. The second glass temperature is detected at $T_{g2} = 250^{\circ}\text{C}$.

In summary, polyphenylene sulfide is thermally very stable. It undergoes interesting and unusual transitions in physical state when heated, which accounts for its good high-temperature mechanical properties. The extruded pellets of polyphenylene sulfide are highly crystalline, with a melting point of 89°C . Crosslinking with

the formation of an amorphous glass occurs at 119°C. The glass temperature of the second glass region is 250° to 271°C.

In the case of polyvinylidene fluoride, the glass transition temperature is at about 40°C. The glassy state is transformed with increasing temperature into a rubbery or elastomeric state. The material melts at about 145°C.

Thermogravimetric Analyses — Thermal analyses of the polymers were conducted on a DuPont 950 thermogravimetric analyzer (TGA) using both nitrogen and air atmospheres with a sample size of 10 mg. The thermogravimetric analysis data of 40°C/min heating rate in nitrogen and in air are shown in Figures 4 through 11.

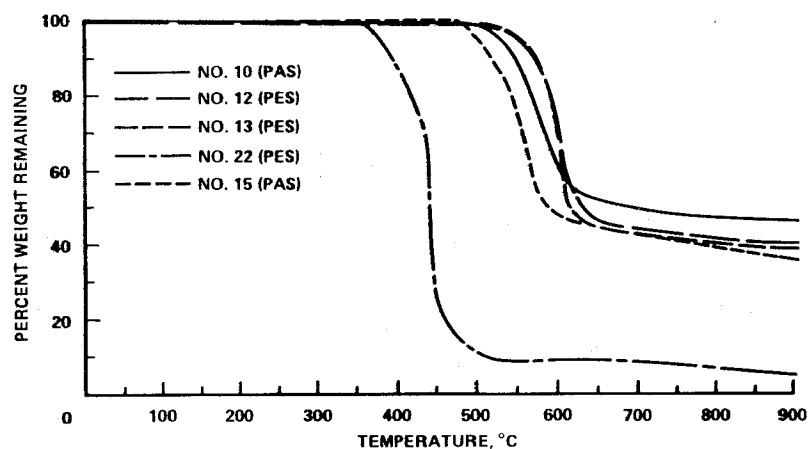


Figure 4. Dynamic thermograph for polyaryl sulfone (PES); polyether sulfone (PAS) (heating rate - 40° C/min, N₂).

The pyrolysis of the samples in air and nitrogen atmospheres was conducted to determine the pyrolysis temperature of the samples in order that similar temperatures be utilized in the furnace used to pyrolyze samples for assessing their relative toxicity as described later in the text. Pyrolysis in an air atmosphere is intended to approximate the environment in the pyrolysis tube at the start of the toxicity test; pyrolysis in a nitrogen atmosphere is intended to approximate the environment in the pyrolysis tube during the test after the original air has been displaced by pyrolysis effluent. The degradation products are continuously removed from the sample during thermogravimetric analysis, and in the relative toxicity test apparatus described later they are conveyed only by normal thermal flow. The TGA data in the nitrogen atmosphere are considered more relevant, because in the toxicity apparatus the pyrolysis effluents that evolved at lower temperature have essentially displaced the original air by the time the temperature has reached 800°C.

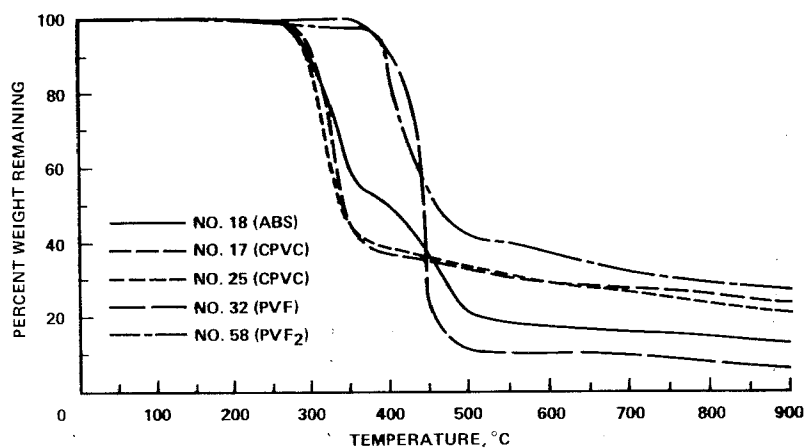


Figure 5. Dynamic thermograph for acrylonitrile butadiene styrene (ABS); chlorinated polyvinyl chloride homopolymer (CPVC); polyvinyl fluoride (PVF); and polyvinylidene fluoride (PVF₂) (heating rate = 40° C/min, N₂).

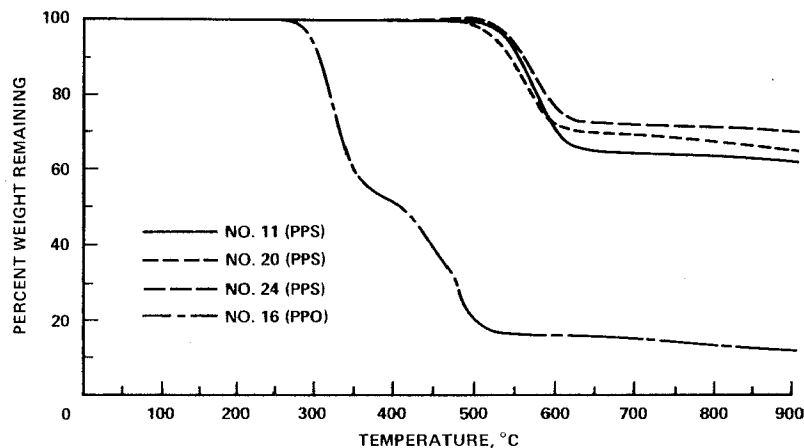


Figure 6. Dynamic thermograph for polyphenylene sulfide (PPS); and polyphenylene oxide (PPO) (heating rate = 40° C/min, N₂).

All thermoplastics underwent thermooxidative decomposition in two major steps, which is characteristic of polymeric materials.

9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer (samples 21, 23, 27 and 28) is the most stable transparent thermoplastic polymer and gives the highest char yield in nitrogen and air. Polyphenylene sulfide (samples 11, 20, and 24) is the most stable polymer tested in both the

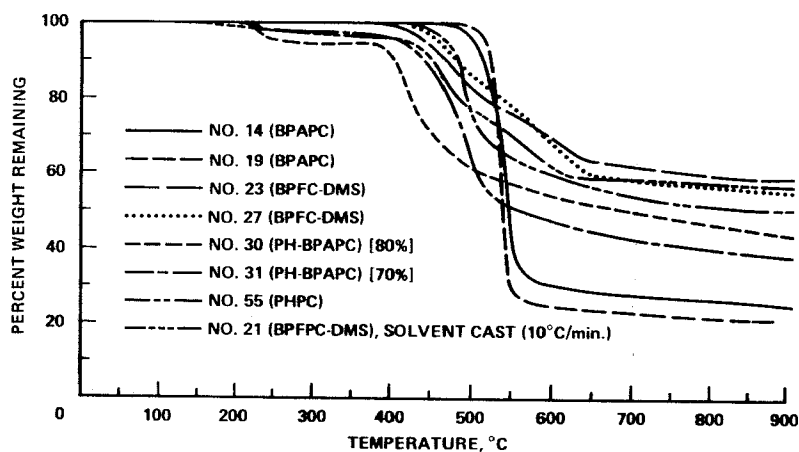


Figure 7. Dynamic thermograph for bisphenol A polycarbonate (BPAPC); 9, 9 bis (hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer (BPFC-DMS); phenolphthalein-bisphenol A polycarbonate copolymer (PH-BPAPC) and phenolphthalein polycarbonate (PHPC) (heating rate = 40°C/min, N_2).

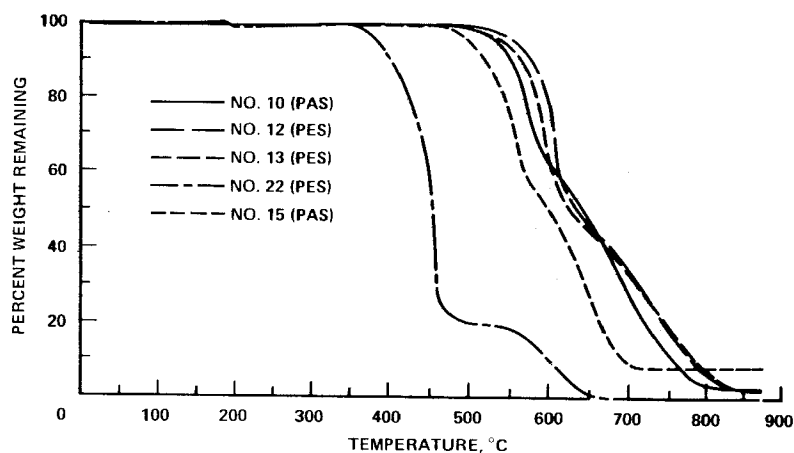


Figure 8. Dynamic thermograph for polyaryl sulfone (PAS) and polyether sulfone (PES) (heating rate = 40°C/min, air).

anaerobic and oxidative environments. According to previous studies [32], thermo-oxidative degradation of polyphenylene sulfide occurs rapidly above 520°C. This is in excellent agreement with the present studies, during which degradation occurred at approximately 500°C.

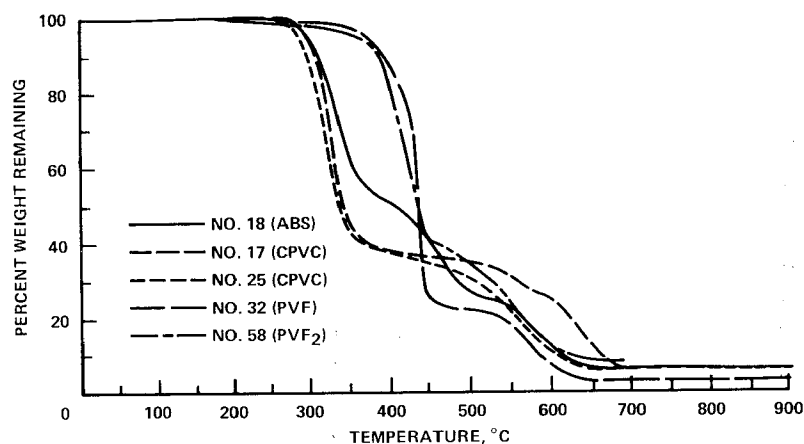


Figure 9. Dynamic thermograph for acrylonitrile butadiene styrene (ABS); chlorinated polyvinyl chloride, homopolymer (CPVC); polyvinyl fluoride (PVF); and polyvinylidene fluoride (PVF₂) (heating rate = 40° C/min, air).

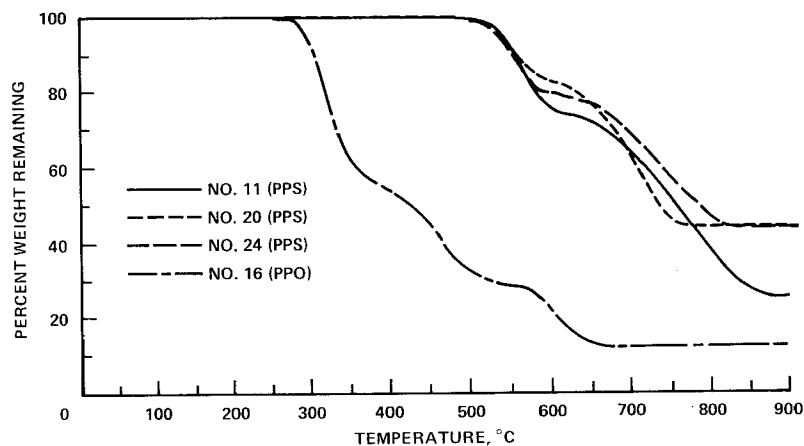


Figure 10. Dynamic thermograph for polyphenylene sulfide (PPS); and polyphenylene oxide (PPO) (heating rate = 40° C/min, air).

Physical Properties

Some of the physical properties of the polymers are shown in Table 4. Properties that were evaluated included specific gravity, tensile strength, ultimate elongation, heat deflection temperature, flexural strength, flexural modulus, impact strength, and compressive strength. Phenolphthalein-bisphenol A polycarbonate copolymer

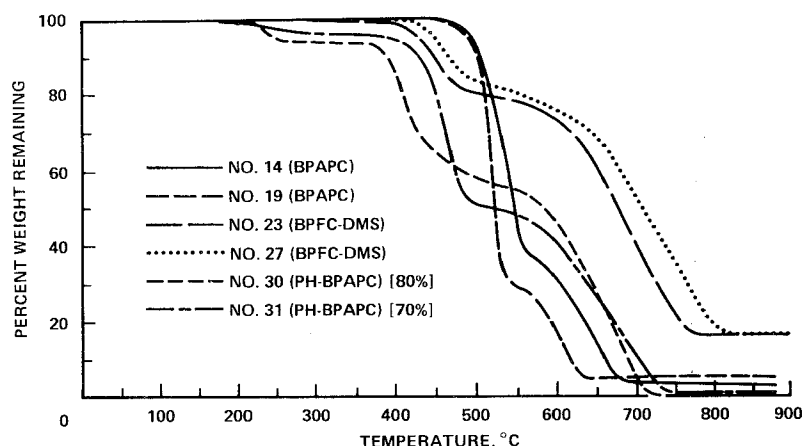


Figure 11. Dynamic thermograph for bisphenol A polycarbonate (BPAC); 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer (BPFC-DMS); phenolphthalein-bisphenol A polycarbonate copolymer (PH-BPAPC) (heating rate = 40° C/min, air).

was not available in sufficient quantity to permit mechanical testing. The physical properties of the advanced polymers are within the range of the desired properties of thermoplastic materials for aircraft interior components [34].

Flammability Properties

Oxygen Index — The oxygen index of the polymers were determined per ASTM D-2863 and is shown in Table 5. Polyphenylene sulfide, 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer and chlorinated polyvinyl chloride had the highest oxygen index of the polymers tested.

Smoke Evolution — Smoke evolution from the polymers was determined using the NBS-Aminco smoke density chamber. The procedure and test method used were essentially those described by NFPA-258-T [35]. A detailed description of the NBS smoke chamber can be found in Reference 36. The D_s values are obtained from individual test data and then averaged. The test results obtained are presented in Tables 6 and 7. Tests were conducted at a heat flux of 2.5 W/cm² under flaming and smoldering conditions. Of the state-of-the-art materials, polyvinyl fluoride has an extremely low smoke evolution. Of the advanced materials, polyvinylidene fluoride has the lowest smoke evolution. The low smoke evolution of PVF was caused by the thin film utilized in this test. The film was consumed very rapidly upon application of the pilot flame. Similar smoke tests conducted by another laboratory [34] utilizing thicker PVF films indicated a specific optical density of 58 in 4 min. 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block

Table 4. Continued.

SAMPLE NUMBER	POLYMER	PROPERTIES							
		SPECIFIC GRAVITY ASTM D792 (g/cm ³)	TENSILE STRENGTH @ 23 °C ASTM D1708 (MN/m ²)	ULTIMATE ELONGATION @ 23 °C ASTM D1708 (%)	HEAT DEFLECTION TEMPERATURE @ 182 KN/m ² ASTM D648 (°C)	FLEXURAL STRENGTH @ 23 °C ASTM D790 (MN/m ²)	FLEXURAL MODULUS @ 23 °C ASTM D790 (GN/m ²)	IMPACT STRENGTH (NOTCHED Izod) @ 23 °C ASTM D256 (J/m)	COMPRESSIVE STRENGTH @ 23 °C ASTM D1621-64 (GN/m ²)
10	POLYARYL SULFONE (PAS)	1.25	68.95	40	166.0	103.43	2.34	69.4	93.08
15		1.37	41.37	20	93.0	65.50	1.72	266.9	---
17	CHLORINATED POLYVINYL CHLORIDE HOMO- POLYMER (CPVC)	1.60	34.48	30	82.2	65.50	1.72	266.9	---
25		1.60	34.48	30	82.2	65.50	1.72	266.9	---
32	POLYVINYL FLUORIDE (PVF)	1.38-1.57	48.27-68.95	115-225	107.0	---	---	---	---
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	1.75-1.80	42.06-58.61	50-100	141-168	---	1.38	138.8-202.9	68.95

Table 5. Oxygen Index for Polymers.

SAMPLE NUMBER	POLYMER	OXYGEN INDEX AT 23°C, ASTM D-2863
18	ACRYLONITRILE BUTADIENE STYRENE (ABS)	34.5
14	BISPHENOL A POLYCARBONATE (BPAPC)	32.0
19		33.5
21	9,9 BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYL-SILOXANE) BLOCK POLYMER (BPFC-DMS)	29.0-32.0
23		47.5
27		
28	PHENOLPHTHALEIN-BISPHENOL A POLYCARBONATE COPOLYMER (PH-BPAPC)	
30		38.0
31		26.8
55	PHENOLPHTHALEIN POLYCARBONATE (PHPC)	32.0
12	POLYETHER SULFONE (PES)	40.5
13		40.0
22		30.0
16	POLYPHENYLENE OXIDE (PPO)	32.0
11	POLYPHENYLENE SULFIDE (PPS)	48.0
20		48.0
24		50.0
10	POLYARYL SULFONE (PAS)	36.0
15		30.0
17	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	55.0
25		55.0
32	POLYVINYL FLUORIDE (PVF)	16.0-20.0
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	43.4

polymer also exhibited low smoke evolution. Phenolphthalein-bisphenol A polycarbonate copolymer and phenolphthalein polycarbonate were not available in sufficient quantity to permit determination of the smoke evolution.

Relative Toxicity – The relative toxicity of the pyrolysis effluents of the thermoplastic materials was determined. The methodology and apparatus utilized for assessing the relative toxicity of the pyrolysis effluents has been described previously [37-44]. A summary of the procedure is as follows.

Four Swiss albino mice are placed in an animal exposure chamber (4.2 liter vol.) and given a minimum of 5 min to adjust to their surroundings. With both sample and animals in place, the entire system is sealed and all joints checked for proper sealing. The animal exposure chamber is the last part sealed, to minimize oxygen consumption before the actual start of test. The furnace is preheated to 200°C and, at the start of the test, is turned on at the predetermined heating rate of 40°C/min.

Table 6. Smoke Evolution from Thermoplastics (NBS Smoke Chamber, 2.5 W/cm², Flaming).

SAMPLE NUMBER	POLYMER	SPECIFIC OPTICAL DENSITY			TIME (min, sec)
		D _s AT 1.5 min.	D _s AT 4.0 min.	D _m (max.)	
18	ACRYLONITRILE BUTADIENE STYRENE (ABS)	175.58	605.54	687.09	8:15
		179.68	652.45	921.06	6:15
		172.46	638.67	921.06	6:00
		AVG. 175.90 ± 3.61	632.22 ± 23.46	843.07 ± 116.98	6:50 ± 1:08
14	BISPHENOL A POLYCARBONATE (BPAPC)	19.57	336.93	345.91	4:30
		17.21	352.34	366.12	5:00
		9.96	355.42	376.33	4:30
		AVG. 15.58 ± 4.81	348.23 ± 9.25	362.72 ± 15.21	4:40 ± 0:15
19		28.06	97.99	182.39	20:00
		38.25	116.59	204.53	17:30
		17.36	62.67	174.60	16:00
		AVG. 27.89 ± 10.45	92.41 ± 26.96	187.17 ± 14.97	17:50 ± 2:00
21		---	---	---	---
23	9,9 BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYLSILOXANE) BLOCK POLYMER (BPFC-DMS)	9.69	71.73	225.00	13:00
		12.04	63.35	196.16	18:00
		AVG. 10.87 ± 1.18	67.54 ± 4.19	210.58 ± 7.50	15:30 ± 2:30
		---	---	---	---
27		---	---	---	---
28		---	---	---	---
30	PHENOLPHTHALEIN-BISPHENOL A POLYCARBONATE COPOLYMER (PH-BPAPC)	---	---	---	---
		---	---	---	---
		---	---	---	---
		---	---	---	---

Table 6. Continued.

SAMPLE NUMBER	POLYMER	SPECIFIC OPTICAL DENSITY				TIME (min., sec.)
		D _s AT 1.5 min.	D _s AT 4.0 min.	D _m (max.)		
55	PHENOLPHTHALEIN POLY-CARBONATE (PHPC)	---	---	---	---	
12	POLYETHER SULFONE (PES)	0.17	2.21	44.13	20:00	
		0.11	1.62	63.70	20:00	
		0.52	2.16	60.48	20:00	
13		AVG. 0.27 ± 0.21	2.00 ± 0.30	56.10 ± 9.79	20:00 ± 1:00	
22		---	---	---	---	
16	POLYPHENYLENE OXIDE (PPO)	248.17	577.27	647.48	5:15	
		240.00	687.09	921.06	4:15	
		256.68	647.49	697.57	4:45	
11		AVG. 248.28 ± 8.34	637.27 ± 54.91	755.35 ± 136.79	4:75 ± 0:30	
20	POLYPHENYLENE SULFIDE (PPS)	---	---	---	---	
		0.00	7.83	110.35	19:30	
		0.23	17.59	132.15	15:30	
24		0.11	14.35	132.15	12:00	
		AVG. 0.11 ± 0.06	13.26 ± 4.88	124.88 ± 10.9	15:40 ± 3:45	
		---	---	---	---	

Table 6. Continued.

SAMPLE NUMBER	POLYMER	SPECIFIC OPTICAL DENSITY			TIME (min., sec.)
		D _s AT 1.5 min.	D _s AT 4.0 min.	D _m (max.)	
10		---	---	---	---
15	POLYARYL SULFONE (PAS)	4.77	19.33	236.66	28:00
		3.17	21.87	277.87	20:00
		4.02	76.98	208.56	10:30
		AVG. 3.99 ± 0.79	39.8 ± 28.83	241.03 ± 34.66	15.43 ± 5.25
17	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	164.73	375.51	376.33	4:15
		140.20	321.70	352.62	6:00
		166.79	336.72	336.72	4:00
25		AVG. 157.24 ± 13.30	344.64 ± 26.91	355.22 ± 19.81	4:45 ± 1:00
		---	---	---	---
32	POLYVINYL FLUORIDE (PVF)	0.57	0.52	0.86	0:15
		0.34	1.21	4.89	13:13
		0.98	0.99	1.21	0:45
		AVG. 0.63 ± 0.32	0.91 ± 0.35	2.32 ± 2.01	4:50 ± 6:38
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	10.65	15.01	16.36	7:45
		8.62	16.36	21.29	10:30
		AVG. 9.64 ± 1.02	15.19 ± 0.68	18.83 ± 2.47	9:08 ± 1:23

Table 7. Smoke Evolution from Thermoplastics (NBS Smoke Chamber, 2.5 W/cm², Smoldering.)

SAMPLE NUMBER	POLYMER	SPECIFIC OPTICAL DENSITY			TIME (min., sec.)
		D _s AT 1.5 min.	D _s AT 4.0 min.	D _m (max.)	
18	ACRYLONITRILE BUTADIENE STYRENE (ABS)	32.42	243.53	463.16	12:30
		26.49	240.76	488.75	10:00
		26.77	220.48	476.28	11:00
		AVG. 28.23	235.26	476.07	11:10
14	BISPHENOL A POLYCARBONATE (BPAPC)	0.23	0.40	13.54	20:00
		0.23	0.46	18.69	20:00
		0.29	0.57	10.57	20:00
		AVG. 0.25	0.48	14.27	20:00
19		0.23	0.46	38.48	20:00
		0.23	0.52	86.78	20:00
		0.17	0.46	45.50	20:00
		AVG. 0.21	0.48	56.92	20:00
16	POLYPHENYLENE OXIDE (PPO)	76.98	319.21	749.87	5:15
		97.98	320.29	457.58	9:15
		68.42	262.59	394.17	9:15
		AVG. 81.12	300.10	533.87	7:55
15	POLYARYL SULFONE (PAS)	1.10	3.54	10.58	20:00
		0.86	3.41	13.62	20:00
		0.98	4.84	12.04	20:00
		AVG. 0.96	3.86	12.08	20:00
17	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	19.49	54.84	135.06	18:00
		27.32	82.27	171.08	14:00
		26.68	84.48	166.68	12:00
		AVG. 24.50	73.86	157.58	14:40

When the upper temperature limit of 800°C is approached or reached, this temperature is maintained by either automatic or manual control until the end of the test. The test period is normally 30 min; if 100% mortality occurs in less than 30 min, the test is terminated upon the death of the last surviving animal. It is difficult to choose time to death or time to incapacitation as the criterion of toxicity, because some materials produce incapacitation more rapidly than other materials. Test results are indicated in Tables 8–10.

Chlorinated polyvinyl chloride homopolymer (samples 17 and 25) and polyphenylene oxide (sample 16) appeared to be among the least toxic on the basis of time to death, and among the most toxic on the basis of time to first sign of incapacitation. The choice of time to death or time to incapacitation as the criterion of toxicity evidently affects rankings of relative toxicity. Bisphenol A polycarbonate (sample 14) appeared to be the least toxic on the basis of time to death.

Similar studies were conducted to determine the apparent lethal concentration (ALC_{50}) produced from the pyrolysis effluents of these materials. The methodology utilized for these tests has been described previously [44]. The same heating rates were utilized as above. The results of these tests are indicated in Tables 11–12. 9,9 bis (4-hydroxyphenyl) fluorene polycarbonate-poly (dimethylsiloxane) block polymer was the least toxic material when tested in this manner.

Effect of Char Yield on Oxygen Index — Previous studies [45] have shown a correlation between the flammability properties of some polymers and their char yield. Figure 12 compares the oxygen index of the polymers evaluated with their relative anaerobic char yield. It can be seen that, in general, polymers with high char yield exhibit a high oxygen index. Chlorinated polyvinyl chloride homopolymer (samples 17 and 25) exhibit a high oxygen index and a relatively low char yield. Previous studies [46] have shown that the principal combustion product of this polymer from ambient to 350°C are hydrogen chloride and benzene. The mole ratio of hydrogen chloride to benzene was 2.5:1 during the initial weight loss (approximately 63% weight loss from ambient to 350°C). This is equivalent to 0.539 g of HCl per 1.0 g of initial sample of polymer combusted. It is known [47] that HCl is a flame inhibitor and the high oxygen index is attributed to the quenching effect of the HCl during the test.

CONCLUSION

The flammability properties of the polymers evaluated are summarized in Table 13. The relative flammability characteristics of these polymers are indicated in Table 14. For comparative purposes, the values of the material properties are indicated in terms of percent, 100% indicating the most desirable fire-safe material properties. The problem of evaluation of materials in terms of fire safety is complex. To rank materials, it would be desirable to develop a "fire safety equation" that would assign weight to specific measurements of each variable, i.e., oxygen index, smoke evolution, toxicity of the oxidative pyrolysates, and thermal stability

Table 8. Relative Toxicity of Degradation Products of Polymers.

SAMPLE NUMBER	POLYMER	Wc (g)	Wp (g)	M10 (%)	M20 (%)	M30 (%)	Ti (min.)	Td (min.)	Tc (max.)	% O2 (min.)	Tr (max.)
18	ACRYLONITRILE BUTADIENE STYRENE (ABS)	1.0002	0.8613	0	25	100	10.42	22.31 ± 5.48	28.0	15.5	791
		1.0007	0.8551	0	100	100	12.28	16.30 ± 0.72	25.0	16.5	690
		MEAN		0	62	100	11.35 ± 1.32	19.30 ± 4.25			
14	BISPENOL A POLYCARBONATE (BPAPC)	1.0009	0.8920	0	75	100	14.70	19.33 ± 1.09	26.5	15.1	787
		1.0001	0.8731	0	0	100	17.33	26.75 ± 2.44	25.2	13.8	786
		MEAN		0	38	100	16.02 ± 1.86	23.04 ± 5.25			
19	BISPENOL A POLYCARBONATE (BPAPC)	1.0000	0.8419	0	75	100	14.78	18.90 ± 1.90	26.0	15.8	789
		1.0008	0.8263	0	100	100	10.87	13.27 ± 1.15	26.0	16.7	700
		MEAN		0	88	100	12.82 ± 2.76	16.08 ± 3.98			
23	9,9-BIS(4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYLSILOXANE) BLOCK POLYMER (BPFC-DMS)										
		0.9997	0.4314	0	50	100	16.77	20.52 ± 1.96	26.0	15.3	810
31	PHENOLPHTHALEIN-BISPENOL A POLYCARBONATE COPOLYMER (PH-BPAPC)	1.0054	0.6201	0	100	100	14.15	16.92 ± 0.13	24.0	17.2	720
12	POLYETHER SULFONE (PES)	1.0001	0.5607	0	100	100	10.65	12.12 ± 0.62	25.5	16.4	638
		1.0027	0.5701	50	100	100	8.56	10.22 ± 0.52	27.5	16.6	630
		1.0010	0.5670	0	100	100	10.83	12.67 ± 0.89	27.0	15.5	690
13	POLYETHER SULFONE (PES)	1.0007	0.5583	12	100	100	12.83	13.88 ± 0.18	25.5	16.6	630
		MEAN					10.72 ± 1.74	12.22 ± 1.52			
22	POLYETHER SULFONE (PES)	0.9999	0.5860	0	100	100	11.78	12.77 ± 0.56	26.5	16.6	650
		1.0001	0.5820	0	100	100	15.00	16.08 ± 0.67	26.0	15.6	
		MEAN		0	100	100	13.39 ± 2.28	14.42 ± 2.23			
16	POLYPHENYLENE OXIDE (PPO)	0.9998	0.5574	25	100	100	9.63	10.26 ± 0.32	25.0	19.4	590
		1.0008	0.9256	0	25	100	7.03	22.51 ± 4.26	26.5	14.2	783
		MEAN		0	62	100	10.27	17.40 ± 0.26	26.0	16.5	800
				0			8.65 ± 2.29	19.96 ± 3.61			

Table 8. Continued.

SAMPLE NUMBER	POLYMER	Wc (g)	Wp (g)	M10 (%)	M20 (%)	M30 (%)	T _i (min.)	T _d (min.)	T _c (max.)	% O ₂ (min.)	T _f (max.)
11	POLYPHENYLENE SULFIDE (PPS)	0.9998	0.3205	0	100	100	11.17	12.19 ± 0.10	27.5	15.4	672
		1.0059	0.3344	100	100	100	8.83	9.46 ± 0.15	27.0	16.7	660
		1.0004	0.3590	0	100	100	10.10	11.28 ± 0.21	25.7	18.2	640
		0.9798	0.3165	100	100	100	8.26	9.35 ± 0.08	26.0	19.0	570
		MEAN		50	100	100	9.59 ± 1.30	10.57 ± 1.40			
20	POLYPHENYLENE SULFIDE (PPS)	1.0001	0.2659	0	100	100	11.50	12.22 ± 0.72	26.0	16.8	623
		1.0004	0.2592	75	100	100	8.95	9.92 ± 0.36	25.0	16.3	619
		MEAN		38	100	100	10.22 ± 1.80	11.07 ± 1.63			
24	POLYPHENYLENE SULFIDE (PPS)	1.0002	0.2540	0	100	100	12.17	13.71 ± 0.67	27.0	16.5	660
		0.9994	0.2624	0	100	100	9.50	11.08 ± 0.12	26.0	16.3	619
		MEAN		0	100	100	10.84 ± 1.89	12.40 ± 1.86			
10	POLYARYL SULFONE (PAS)	1.0037	0.4995	0	100	100	9.67	10.79 ± 0.53	26.0	16.2	643
		0.9991	0.4852	0	100	100	11.50	12.88 ± 0.37	27.0	15.4	740
		1.0017	0.4806	25	100	100	8.87	10.01 ± 0.14	29.5	17.4	600
		MEAN		8	100	100	10.01 ± 1.35	11.23 ± 1.48			
15	POLYARYL SULFONE (PAS)	0.9998	0.6394	0	100	100	11.55	14.73 ± 0.50	25.5	16.3	693
		1.0001	0.6523	0	75	100	9.67	16.71 ± 4.85	24.3	15.1	788
		MEAN		0	88	100	10.61 ± 1.33	15.72 ± 1.40			
17	CHLORINATED POLYVINYL CHLORIDE HOMO-POLYMER (CPVC)	0.9941	0.7356	0	0	100	6.92	24.64 ± 1.82	28.0	13.2	794
		1.0034	0.7208	0	100	100	6.23	16.92 ± 2.45	27.0	15.4	748
		1.0007	0.7357	0	0	100	5.72	23.72 ± 0.82	27.0	14.6	748
		MEAN		0	33	100	6.29 ± 0.60	21.76 ± 4.22			
25	CHLORINATED POLYVINYL CHLORIDE HOMO-POLYMER (CPVC)	1.0003	0.7240	0	25	100	9.00	22.74 ± 6.22	28.0	15.2	793
32	POLYVINYL FLUORIDE (PVF)	0.9996		0	0	100	18.63	21.95 ± 0.43	26.0	16.5	800
		1.0019		0	75	100	15.25	19.05 ± 0.92	25.2	16.3	800
		MEAN		0	38	100	16.94 ± 2.39	20.50 ± 2.05			
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	1.008	0.808	0	100	100	6.58	17.79 ± 2.11	24.8	15.8	800
		1.020	0.744	0	100	100	6.42	13.92 ± 1.14	25.2	16.6	800
		0.9993	0.7514	0	75	100	14.58	20.31 ± 2.89	25.0	16.2	800
		MEAN		0	91	100	9.19 ± 4.67	17.34 ± 3.22	25.0	10.2	800

Table 9. Relative Toxicity of Degradation Products (Time to Incapacitation).

SAMPLE NUMBER	POLYMER	TIME TO INCAPACITATION (T _i , IN MINUTES)
17	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	6.29 ± 0.60
16	POLYPHENYLENE OXIDE (PPO)	8.65 ± 2.29
25	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	9.00 —
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	9.19 ± 4.67
11	POLYPHENYLENE SULFIDE (PPS)	9.59 ± 1.30
22	POLYETHER SULFONE (PES)	9.63 —
10	POLYARYL SULFONE (PAS)	10.01 ± 1.35
20	POLYPHENYLENE SULFIDE (PPS)	10.22 ± 1.80
15	POLYSULFONE (PAS)	10.61 ± 1.33
12	POLYETHER SULFONE (PES)	10.72 ± 1.74
24	POLYPHENYLENE SULFIDE (PPS)	10.48 ± 1.89
18	ACRYLONITRILE-BUTADIENE-STYRENE (ABS)	11.35 ± 1.32
19	BISPHENOL A POLYCARBONATE (BPAPC)	12.82 ± 2.76
13	POLYETHER SULFONE (PES)	13.39 ± 2.28
31	PHENOLPHTHALEIN-BISPHENOL A POLYCARBONATE COPOLYMER (PHBPA PC)	14.15 —
14	BISPHENOL A POLYCARBONATE (BPAPC)	16.02 ± 1.86
23	9,9, BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYL-SILOXANE) BLOCK POLYMER (BPFC-DMS)	16.77 —
32	POLYVINYL FLUORIDE (PVF)	16.94 ± 2.39

(char yield) of each polymer. Development of such an equation is dependent on: identification of the variables (OI, D, %Ti, %Td, Yc), determination of the importance of each variable to the real aircraft fire situation, selection of measurement techniques for each variable and determination of the weight to be assigned to the measurement of each specific variable to reflect the real fire situation. It is beyond the scope of this study to define such an equation, but some general conclusions may be drawn based on the data presented in Table 14. Assuming equal weight assignment to each flammability parameter and averaging the percent values indicated, the polymers and their relative percent values could be rated as follows, in order of increased fire safety: polyphenylene oxide (sample 16) 28%; acrylonitrile butadiene styrene (sample 18) 30.1%; bisphenol A polycarbonate (sample 19) 32.5%; chlorinated polyvinyl chloride homopolymer (sample 17) 35.5%; bisphenol A polycarbonate (sample 14) 37.7%; polyaryl sulfone (sample 15) 42.4%; poly-

Table 10. Relative Toxicity of Degradation Products (Time to Death).

SAMPLE NUMBER	POLYMER	TIME TO DEATH (T _d , IN MINUTES)
22	POLYETHER SULFONE (PES)	10.26 ± 0.32
11	POLYPHENYLENE SULFIDE (PPS)	10.57 ± 1.40
20	POLYPHENYLENE SULFIDE (PPS)	11.07 ± 1.63
10	POLYARYL SULFONE (PAS)	11.23 ± 1.48
12	POLYETHER SULFONE (PES)	12.22 ± 1.52
24	POLYPHENYLENE SULFIDE (PPS)	12.04 ± 1.86
13	POLYETHER SULFONE (PES)	14.42 ± 2.34
15	POLYSULFONE (PAS)	15.72 ± 1.40
19	BISPHENOL A POLYCARBONATE (BPACPC)	16.08 ± 3.98
31	PHENOLPHTHALEIN-BISPHENOL A POLYCARBONATE COPOLYMER (PHBPA-PC)	16.92 ± 0.31
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	17.34 ± 3.22
18	ACRYLONITRILE-BUTADIENE-STYRENE (ABS)	19.30 ± 4.25
16	POLYPHENYLENE OXIDE (PPO)	19.96 ± 3.61
32	POLYVINYL FLUORIDE	20.50 ± 2.05
23	9,9, BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYL-SILOXANE) BLOCK POLYMER (BPFC-DMS)	20.52 ± 1.96
17	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	21.76 ± 4.22
25	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER (CPVC)	22.74 ± 6.22
14	BISPHENOL A POLYCARBONATE (BPAPC)	23.04 ± 5.25

vinylidene fluoride (sample 58) 47.4%; polyvinyl fluoride (sample 32) 51.1%; polyether sulfone (sample 12) 51.3%; 9,9 bis (4-hydroxyphenol) fluorene polycarbonate-poly (dimethylsiloxane) block polymer (sample 23) 52.1%; and polyphenylene sulfide (sample 20) 53.0%. The polyvinyl fluoride film (sample 32) would have normally shown lower in the scale of fire-resistant polymers, except that low Ds numbers were obtained during the smoke tests, since the film was consumed early in the tests.

A correlation was established between the oxygen indices of the polymers and their anaerobic char yield. Generally, polymers with high anaerobic char yield exhibited high oxygen index. There was no relationship noted between the thermo-mechanical (T_g, T_m) properties of the polymers and their flammability characteristics.

Table 11. Apparent Lethal Concentrations of Pyrolysis Products of some Thermoplastic Polymers (ALC_{50}).

BASED ON WEIGHT OF SAMPLE LOST			
SAMPLE NUMBER	POLYMER	mg/l	% WEIGHT REMAINING
20	POLYPHENYLENE SULFIDE	11.4 ± 1.1	56.82
24	POLYPHENYLENE SULFIDE	13.3 ± 1.7	59.22
11	POLYPHENYLENE SULFIDE	13.5 ± 1.2	56.45
14	BISPHENOL A POLYCARBONATE	14.4 ± 4.1	4.00
15	POLYARYL SULFONE	14.8 ± 1.2	10.84
	9,9, BIS (4-HYDROXYPHENYL) FLUORENE		
27	POLYCARBONATE-POLY (DIMETHYL-SILOXANE) BLOCK POLYMER (BPFC-DMS)	16.3 ± 1.5	52.06
10	POLYARYL SULFONE	16.9 ± 0.5	21.03
12	POLYETHER SULFONE	17.3 ± 0.4	21.72
18	ACRYLONITRILE-BUTADIENE-STYRENE	20.3 ± 0.8	5.14
17	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER	22.8 ± 6.0	3.39
13	POLYETHER SULFONE	23.1 ± 2.1	23.26
16	POLYPHENYLENE OXIDE	28.5 ± 8.7	16.18
19	BISPHENOL A POLYCARBONATE	29.9 ± 1.7	7.72
25	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER	31.9 ± 0.1	10.86
58	POLYVINYLIDENE FLUORIDE	78.2 ± 5.0	20.69
	9,9, BIS (4-HYDROXYPHENYL) FLUORENE		
28	POLYCARBONATE-POLY (DIMETHYL-SILOXANE) (BPFC-DMS)	93.2 ± 2.0	59.91

SYMBOLS AND ABBREVIATIONS

ALC_{50} apparent lethal concentration; mg of sample (charged in furnace or lost during pyrolysis) per liter of animal chamber volume required to cause 50% of test animal deaths

$$D = \text{percent light transmittance} = \frac{100}{\text{antilog} \left(\frac{D_s}{132} \right)} = \frac{100}{10^{(D_s/132)}}$$

D_m specific optical density, max

D_s specific optical smoke density = $132 \log_{10} \left(\frac{100}{D} \right)$

M10 Mortality after 10 min exposure, %

M20 mortality after 20 min exposure, %

Table 12. Apparent Lethal Concentrations of Pyrolysis Products of some Thermoplastic Polymers.

BASED ON WEIGHT CHARGED		
SAMPLE NUMBER	POLYMER	mg/l
14	BISPHENOL A POLYCARBONATE	15.0 ± 4.3
15	POLYARYL SULFONE	16.6 ± 2.8
18	ACRYLONITRILE-BUTADIENE-STYRENE	21.4 ± 0.9
10	POLYARYL SULFONE	21.8 ± 2.5
12	POLYETHER SULFONE	22.1 ± 0.8
17	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER	23.6 ± 4.0
20	POLYPHENYLENE SULFIDE	26.4 ± 2.9
13	POLYETHER SULFONE	30.1 ± 3.1
11	POLYPHENYLENE SULFIDE	31.0 ± 5.8
19	BISPHENOL A POLYCARBONATE	32.4 ± 0.9
24	POLYPHENYLENE SULFIDE	33.1 ± 4.6
16	POLYPHENYLENE OXIDE	34.0 ± 11.7
27	9,9, BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYL-SILOXANE) BLOCK POLYMER (BPFC-DMS)	34.4 ± 1.6
25	CHLORINATED POLYVINYL CHLORIDE HOMOPOLYMER	35.9 ± 0.6
58	POLYVINYLIDENE FLUORIDE	98.6 ± 7.4
28	9,9, BIS (4-HYDROXYPHENYL) FLUORENE POLYCARBONATE-POLY (DIMETHYL-SILOXANE) BLOCK POLYMER (BPFC-DMS)	232.5 ± 8.5

M30 mortality after 30 min exposure, %

OI oxygen index, $\frac{O_2}{O_2 + N_2}$

%O₂ concentration of oxygen in animal exposure chamber, vol. %

T upper temperature limit of pyrolysis, °C

Tc temperature in animal exposure chamber, °C

Td time to death, min

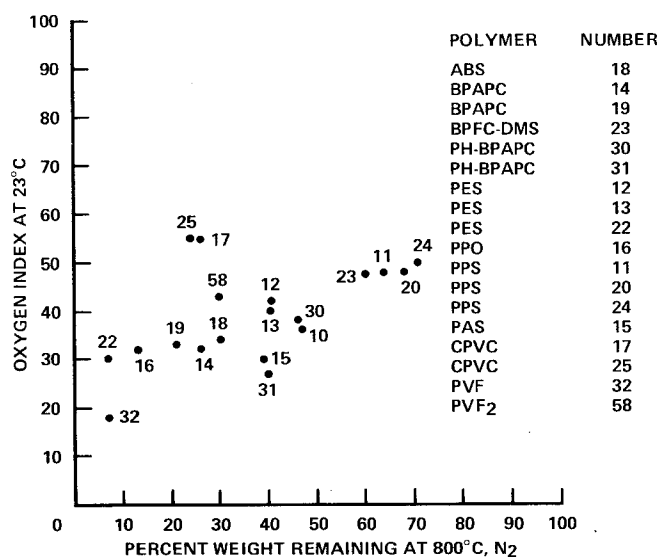
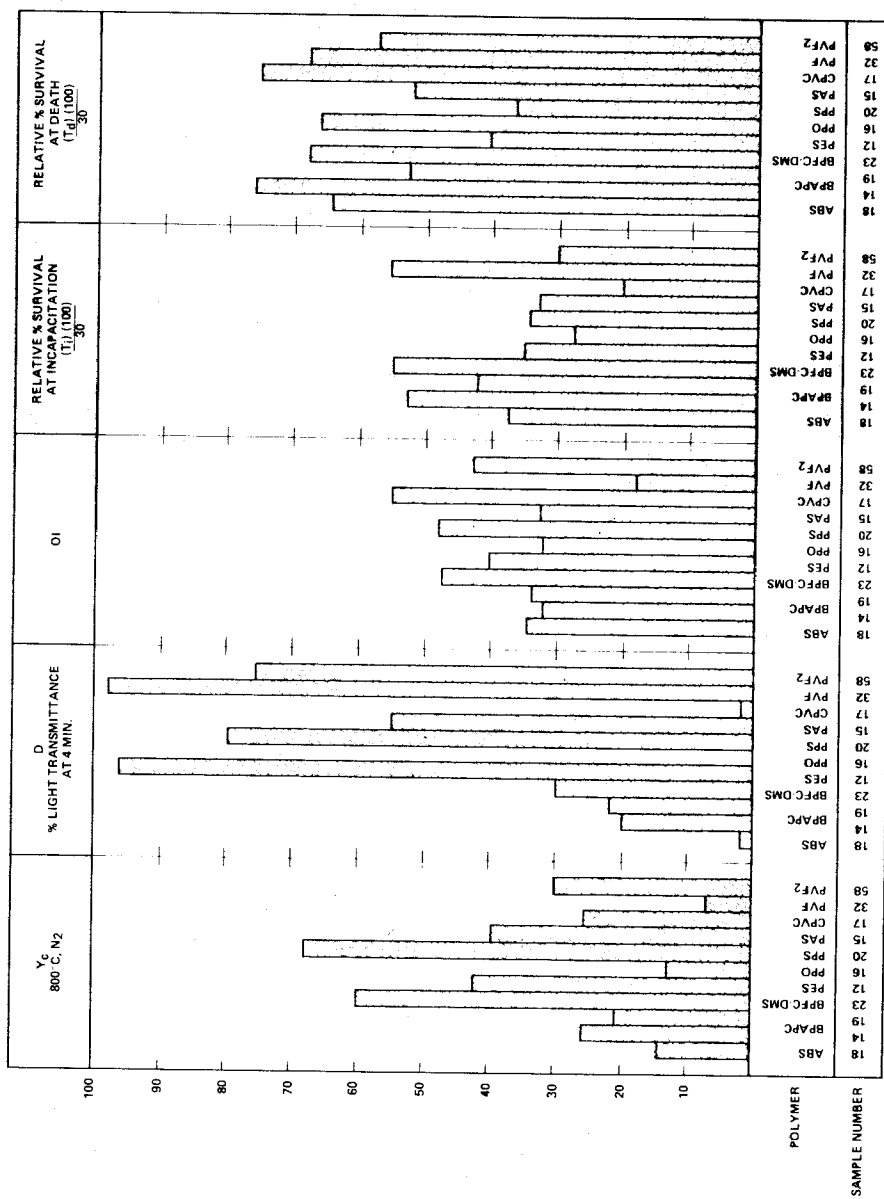


Figure 12. Effect of char yield of thermoplastic polymers on oxygen index.

Table 13. Summary of Flammability Properties of Polymers.

SAMPLE NUMBER	POLYMER	Y _c 800°C, N ₂	OI	D _m	T _i	T _d
18	ACRYLONITRILE BUTADIENE STYRENE (ABS)	14	34.5	843.07	11.35	19.30
14	BISPHENOL A POLYCARBONATE (BPAPC)	26	32.0	362.72	16.02	23.04
19		21	33.5	187.17	12.82	16.08
21	9,9 BIS (4-HYDROXYPHENOL) FLUORENE POLYCARBONATE-POLY (DIMETHYL-SILOXANE) BLOCK COPOLYMER (BPFC-DMS)	---	30.5	---	---	---
23		60	47.5	210.58	16.77	20.52
27		67	---	---	---	---
28		---	---	---	---	---
30	PHENOLPHTHALEIN-BISPHENOL A POLYCARBONATE COPOLYMER (PH-BPAPC)	46	38.0	---	---	---
31		41	26.8	---	14.15	16.92
55	PHENOLPHTHALEIN POLYCARBONATE (PHPC)	---	32.0	---	---	---
12	POLYETHER SULFONE (PES)	42	40.5	56.10	10.72	12.22
13		40	40.0	---	13.39	14.42
22		7	30.0	---	9.63	10.28
16	POLYPHENYLENE OXIDE (PPO)	13	32.0	775.35	8.65	19.96
11		64	48.0	---	9.59	10.57
20	POLYPHENYLENE SULFIDE (PPS)	68	48.0	124.88	10.22	11.07
24		62	50.0	---	10.84	12.40
10	POLYARYL SULFONE (PAS)	47	36.0	---	10.01	11.23
15		39	30.0	241.03	10.61	15.72
17	CHLORINATED POLYVINYL CHLORIDE (CPVC)	26	55.0	355.22	6.29	21.76
25		24	55.0	---	9.00	22.74
32	POLYVINYL FLUORIDE (PVF)	7	18.0	2.32	16.94	20.50
58	POLYVINYLIDENE FLUORIDE (PVF ₂)	30	43.4	18.83	9.19	17.34

Table 14. Relative Flammability Characteristics of Thermoplastics.



% Td	relative percent survival at death; $\% Td = \frac{(100) (Td)}{30}$
Tf	temperature of pyrolysis furnace, °C
Tg	glass transition temperature
Ti	time to first sign of incapacitation, min
% Ti	relative percent survival at incapacitation; $\% Ti = \frac{(100) (Ti)}{30}$
Tm	melt temperature
Wc	weight of sample charged, g
Wp	weight of sample pyrolyzed, g
Yc	char yield or percent weight remaining

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REFERENCES

1. Department of Transportation, Federal Aviation Administration, Airworthiness Standards: Transport Category Airplanes, Federal Aviation Regulations, Vol. III, Part 25, Transmittal 10, effective May 1, 1972.
2. Department of Transportation, Federal Aviation Administration; Notice 75-31: Aircraft, Engine and Propeller, Airworthiness, and Procedural Proposals; Federal Register, Vol. 40, June 11, 1975.
3. Department of Transportation, Federal Aviation Administration, Flight Standard, Service, Transport Category Airplanes; Notice 75-3. Smoke Emission from Compartment Interior Materials; Federal Register, Vol. 40, p. 6505, February 12, 1975.
4. Department of Transportation, Federal Aviation Administration, Flight Standards Service, Notice 74-38, Compartment Interior Materials: Toxic Gas Emission; Federal Register, Vol. 39, p. 45044, December 30, 1974.
5. "Flaming and Self-Extinguishing Characteristics of Aircraft Cabin Interior Materials," FAA Final Report No. NA-68-30 (DS-68-13), July 1968.
6. D. Gross, J. J. Loftus, T. G. Lee, and V. E. Gray, "Smoke and Gases Produced by Burning Aircraft Interior Materials," Federal Aviation Administration Report No. NA-68-36 (DS-68-16), June 1968.
7. D. R. Mott, W. W. Spruance, D. Danaher, R. McGuire, D. A. Kourtides, A. Bigelow, and R. Ault, "Cabin Interiors - Smoke and Fire," Proceedings of the 12th Annual Conference and Trade Exhibit of the Survival and Flight Equipment Association, September 1974, pp. 114-120.
8. D. Gross, "Smoke and Gases Produced by Burning Interior Materials," NBS Building Science Series 18, February 1968.
9. D. A. Kourtides, J. A. Parker, and W. J. Gilwee, Jr., "Thermochemical Characterization of Aircraft Interior Panel Materials," *J. Fire and Flammability*, Vol. 6, July 1975, pp. 373-391.
10. W. J. Gilwee, J. A. Parker, D. A. Kourtides, and C. J. Hilado, "Fire Resistant Low Density Composites," Proceedings of the ANTEC Meeting, Society of Plastics Engineers, Cleveland, Ohio, Oct. 4-7, 1976.

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11. D. A. Kourtides, J. A. Parker, C. J. Hilado, R. A. Anderson, E. Tustin, D. B. Arnold, J. G. Gaume, A. J. Binding, and J. L. Mikeska, "Fire Safety Evaluation of Aircraft Lavatory and Cargo Compartments," *J. Fire and Flammability*, Vol. 7, January 1976, pp. 125-159.
12. D. A. Kourtides, J. A. Parker, H. A. Leon, R. B. Williamson, H. Hasegawa, F. Fisher, R. Draemel, W. H. Marcussen, and C. J. Hilado, "Fire Containment Tests of Aircraft Interior Panels," *J. Fire and Flammability*, Vol. 7, April 1976, pp. 257-278.
13. C. P. Sarkos, "Measurement of Toxic Gases and Smoke from Aircraft Cabin Interior Materials Using the NBS Smoke Chamber and Colorimetric Tubes," Department of Transportation, Federal Aviation Administration, Report No. FAA-RD-76-7, March 1976, pp. 15-19.
14. Encyclopedia of Polymer Science and Technology, Interscience Publishers Inc., Vol. 13, p. 406.
15. R. P. Kambour, and G. E. Niznik, "Synthesis and Properties of Bisphenol Fluorenone Polycarbonate and BPF Carbonate-Dimethyl Siloxane Block Polymers," Final Report, Contract N00019-72-C-0152, Naval Air Systems Command, Dept. of the Navy, January 1974.
16. R. P. Kambour, J. E. Corn, S. Miller, and G. E. Niznik, "Bisphenol Fluorenone Carbonate-Dimethyl Siloxane Block Polymers: Transparent, Tough, Heat- and Flame-Resistant Thermoplastics," Final Report Contract N00019-74-C-0174, Naval Air Systems Command, TIS Report No. 75CRD230, October 1975.
17. P. C. Juliano, and G. E. Niznik, "High Temperature Block Copolymers - Synthesis and Properties," TIS Report No. 73CRD335, December 1973.
18. P. W. Morgan, "High Temperature Polymers," *Macromolecules*, Vol. 3, p. 536, 1970.
19. J. A. Parker, G. M. Fohlen, and P. M. Sawko, "Development of Transparent Composites and Their Thermal Responses," Proceedings of the USAF Conference on Transparent Aircraft Enclosures, Las Vegas, Nevada, February 1972.
20. D. G. Chasin, and J. Feltzin, "Properties and Applications of Polyether sulfone, A New Family of High Temperature Performance Engineering Thermoplastic," Proceedings of the SAMPE Meeting, Albuquerque, New Mexico, 1975.
21. Encyclopedia of Polymer Science and Technology, Interscience Publishers Inc., Vol. 10, pp. 98-99.
22. J. T. Edmonds, Jr., and H. W. Hill, Jr., U. S. Patent 3,354,129, Phillips Petroleum Co. (November 21, 1967).
23. R. P. Bringer, and G. A. Morneau, "Polymer 360, A New Thermoplastic Polysulfone for Use at 500°C," *Applied Polymer Symposia*, No. 11, 189-208, 1969.
24. C. A. Heimberger, "Chlorinated Vinyl Chloride-Propylene Copolymers for Injection-Moldable High Temperature Vinyls," Proceedings of the 32nd Annual Technical Conference, Society of Plastics Engineers, San Francisco, California, pp. 695-699, May 1974.
25. M. L. Dantris, and F. L. Ramp, U.S. Patent 2,996,489 (August 8, 1961).
26. D. E. Bartrum, Vinyl Technology III (4), December 1970, pp. 18-24.
27. J. T. Stapler et al, "Thermal Degradation of Polyvinylidene Fluoride and Polyvinyl Fluoride by Oven Pyrolysis," U.S. Army Natic Laboratories, Technical Report A067509, July 1968.
28. Encyclopedia of Polymer Science and Technology, Interscience Publishers, Inc., Vol. 3, p. 406.
29. Encyclopedia of Polymer Science and Technology, Interscience Publishers, Inc., Vol. 14, p. 465.
30. T. Honjo, and S. Ogawa, "Kogyo Gijutsuin Seni Kogyo Shinkensho Kenkyo Hokoko," Vol. 1, 1963.
31. J. J. Dietrich, T. E. Hedge, and M. E. Kucsma, "Fire Resistant Coating," *Paint and Varnish Products*, 75, 1966.

32. R. Fish, J. Parker, and G. Fohlen, "Design, Synthesis, and Development of New Transparent Polymers for Military Applications," USAF Conference on Transparent Aircraft Enclosures, Atlanta, Georgia, February 1975.
33. D. G. Brady, "Polyphenylene Sulfide — A Unique Engineering Plastic," Proceedings of the 32nd Annual Technical Conference, Society of Plastic Engineers, San Francisco, California, pp. 684–686, May 1974.
34. B. Silverman, "Development of Fire Resistant, Non-Toxic Aircraft Interior Materials," NASA Final Report NAS2-8835, September 1976.
35. National Fire Protection Association, Bulletin No. NFPA 258-T, 1974.
36. T. G. Lee, Interlaboratory Evaluation of Smoke Density Chamber, National Bureau of Standards Technical Note 708, December 1971.
37. C. J. Hilado, "Evaluation of the NASA Animal Exposure Chamber as a Potential Chamber of Fire Toxicity Screening Tests," *Combustion Toxicology*, Vol. 2, No. 4, November 1975, pp. 298–314.
38. C. J. Hilado, "Relative Toxicity of Pyrolysis Products of Some Foams and Fabrics," *J. Combustion Toxicology*, Vol. 3, No. 1, February 1976, pp. 32–60.
39. C. J. Hilado, "Relative Toxicity of Pyrolysis Products of Some Loose Fiber Materials: A Preliminary Study," *J. Combustion Toxicology*, Vol. 3, No. 2, May 1976, pp. 151–156.
40. C. J. Hilado, and G. H. Damant, "The Effect of Flame Retardants of Properties, Flammability, and Relative Toxicity of Some Conventional Flexible Polyurethane Foams," *J. Fire Retardant Chemistry*, Vol. 3, No. 2, May 1976, pp. 84–98.
41. C. J. Hilado, L. A. LaBossiere, "Evaluation of Some Commercial Materials Using the USF/NASA Fire Toxicity Screening Test Method," *J. Consumer Product Flammability*, Vol. 3, No. 2, June 1976, pp. 141–149.
42. C. J. Hilado, L. A. LaBossiere, H. A. Leon, D. A. Kourtides, J. A. Parker, and M. S. Hsu, "The Sensitivity of Relative Toxicity Rankings by the USF/NASA Test Method to Some Test Variables," *J. Combustion Toxicology*, Vol. 3, No. 3, August 1976, pp. 211–236.
43. C. J. Hilado, and C. M. Miller, "The Effect of Changes in the USF/NASA Fire Toxicity Screening Test Method on Data from Some Cellular Polymers," *J. Combustion Toxicology*, Vol. 3, No. 3, August 1976, pp. 237–258.
44. C. J. Hilado, W. H. Marcussen, A. Furst, D. A. Kourtides, and J. A. Parker, "Apparent Lethal Concentrations of Pyrolysis Products of Some Synthetic Polymers," *J. Combustion Toxicology*, Vol. 3, No. 4, November 1976, pp. 345–362.
45. J. A. Parker, D. A. Kourtides, R. H. Fish, and W. J. Gilwee, "Fire Dynamics of Modern Aircraft from a Materials Point of View," *J. Fire and Flammability*, Vol. 6, October 1976, pp. 534–553.
46. R. W. Mickelson, K. J. Voarhees, and P. W. Ryan, "Correlation Between Thermal Analysis and Effluent Gas Analysis," Polymer Conference Series, University of Utah, July 7–11, 1975.
47. N. R. Lerner, and D. E. Cagliostro, "Flame Inhibition by Hydrogen Halides: Some Spectroscopic Measurement," *J. Combustion and Flame*, Vol. 21, 1973, pp. 315–320.